

Chapter 40 - SANS FROM TERNARY POLYMER BLENDS

A ternary polymer blend is a mixture of three homopolymers. The thermodynamics of mixing and phase separation can be investigated for ternary blends using the SANS technique and the Random Phase Approximation.

1. SANS FROM A TERNARY POLYMER BLEND

Consider a ternary polymer blend consisting of deuterated polystyrene (dPS), non-deuterated polystyrene (hPS) and poly(vinyl methyl ether) (PVME) (Hammouda et al, 1992). The binary blend dPS/PVME is characterized by a Lower Critical Spinodal Temperature (LCST) whereas the binary blend dPS/hPS is characterized by a weak Upper Critical Spinodal Temperature (UCST). Here, the ternary blend was investigated with the goal of testing the RPA model for multi-component mixtures and investigating the phase separation of the binary hPS/PVME blend. This blend does not contain any deuteration and could not be investigated by SANS directly.

A series of three samples was prepared. The characterization of the polymers used and of the volume fractions of the three samples are summarized in two tables.

Table 1: Characterization of the polymers used.

	M_w (g/mol)	M_w/M_n	Degree of Polymerization	Specific Volume (cm ³ /mol)
dPS	$1.95 \cdot 10^5$	1.02	1741	100
hPS	$1.90 \cdot 10^5$	1.04	1827	100
PVME	$1.59 \cdot 10^5$	1.30	2741	55.4

Table 2: Volume fractions for the three samples.

Sample Number	ϕ_{dPS}	ϕ_{PVME}	ϕ_{hPS}
1	0.484	0.516	0
2	0.360	0.511	0.129
3	0.238	0.506	0.256

SANS data were taken from the three samples for a range of temperatures above the polystyrene glass transition temperature (i.e., above 100 °C). SANS data from sample 3 for a range of temperatures in the homogeneous phase region are shown in a figure. The intensity is seen to increase when temperature is increased. This is a sign of LCST behavior.

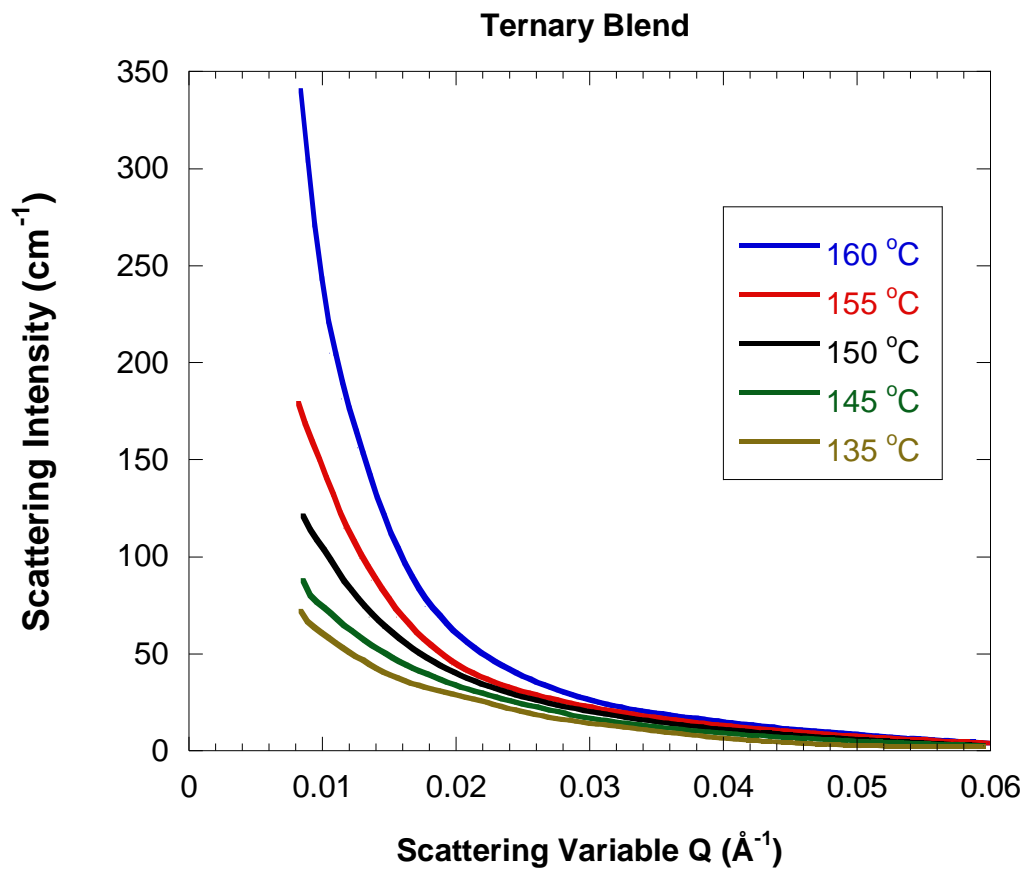


Figure 1: **SANS data** taken from sample 3 for a range of temperatures.

Variation of the **forward scattering intensity** with increasing temperature shows an interesting variation for the 3 samples.

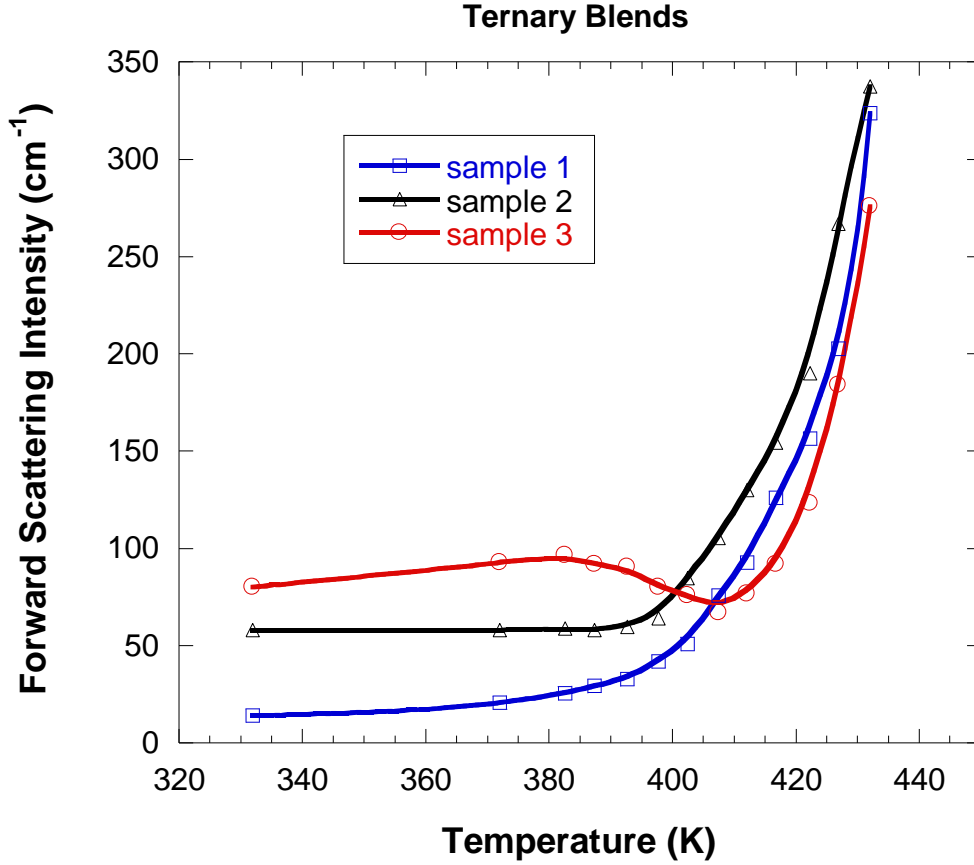


Figure 2: Variation of the forward scattering intensity $d\Sigma(Q=0)/d\Omega$ with increasing temperature for the three ternary blends. The lowest value of $Q = 0.0085 \text{ \AA}^{-1}$ is used to represent the forward scattering value.

Sample 3 shows a decrease in intensity at first then an increase. This is due to the interplay between the LCST behavior for dPS/PVME and hPS/PVME and the UCST behavior for the dPS/hPS.

2. THE TERNARY RPA MODEL

The ternary RPA equations are summarized here. Consider a ternary blend consisting of polymer 1, polymer 2 and polymer 3. The degrees of polymerization are noted n_1 , n_2 and n_3 , the volume fractions are ϕ_1 , ϕ_2 and ϕ_3 , the specific monomer volumes are v_1 , v_2 and v_3 , the radii of gyration are R_{g1} , R_{g2} and R_{g3} , the form factors are $P_1(Q)$, $P_2(Q)$ and $P_3(Q)$ and the Flory-Huggins interaction parameters are χ_{12} , χ_{23} and χ_{13} .

The RPA equations for an incompressible ternary blend in the homogeneous phase are as follows. The non-interacting structure factors are given by:

$$S_{11}^0(Q) = n_1 \phi_1 v_1 P_1(Q) \quad (1)$$

$$S_{22}^0(Q) = n_2 \phi_2 v_2 P_2(Q)$$

$$S_{33}^0(Q) = n_3 \phi_3 v_3 P_3(Q).$$

The form factors are given by the Debye function:

$$P_1(Q) = \frac{2}{Q^4 R_{g1}^4} \left[\exp(-Q^2 R_{g1}^2) - 1 + Q^2 R_{g1}^2 \right] \quad (2)$$

$$P_2(Q) = \frac{2}{Q^4 R_{g2}^4} \left[\exp(-Q^2 R_{g2}^2) - 1 + Q^2 R_{g2}^2 \right]$$

$$P_3(Q) = \frac{2}{Q^4 R_{g3}^4} \left[\exp(-Q^2 R_{g3}^2) - 1 + Q^2 R_{g3}^2 \right].$$

The excluded volume factors are:

$$v_{11}(Q) = \frac{1}{S_{33}^0(Q)} - 2 \frac{\chi_{13}}{v_0} \quad (3)$$

$$v_{22}(Q) = \frac{1}{S_{33}^0(Q)} - 2 \frac{\chi_{23}}{v_0}$$

$$v_{12}(Q) = \frac{1}{S_{33}^0(Q)} + \frac{\chi_{12}}{v_0} - \frac{\chi_{13}}{v_0} - \frac{\chi_{23}}{v_0}.$$

The partial structure factors for the fully interacting mixture are given by:

$$S_{11}(Q) = \frac{S_{11}^0(Q)(1 + v_{22} S_{22}^0(Q))}{(1 + v_{11} S_{11}^0(Q))(1 + v_{22} S_{22}^0(Q)) - v_{12}^2 S_{11}^0(Q) S_{22}^0(Q)} \quad (4)$$

$$S_{22}(Q) = \frac{S_{22}^0(Q)(1 + v_{11} S_{11}^0(Q))}{(1 + v_{11} S_{11}^0(Q))(1 + v_{22} S_{22}^0(Q)) - v_{12}^2 S_{11}^0(Q) S_{22}^0(Q)}$$

$$S_{12}(Q) = \frac{-S_{11}^0(Q) v_{12} S_{22}^0(Q)}{(1 + v_{11} S_{11}^0(Q))(1 + v_{22} S_{22}^0(Q)) - v_{12}^2 S_{11}^0(Q) S_{22}^0(Q)}.$$

The scattering cross section is given by:

$$\frac{d\Sigma(Q)}{d\Omega} = \Delta \rho_1^2 S_{11}(Q) + \Delta \rho_2^2 S_{22}(Q) + 2 \Delta \rho_1 \Delta \rho_2 S_{12}(Q) \quad (5)$$

The relevant contrast factors are:

$$\Delta\rho_1^2 = (\rho_1 - \rho_3)^2 = \left(\frac{b_1}{v_1} - \frac{b_3}{v_3} \right)^2 \quad (6)$$

$$\Delta\rho_2^2 = (\rho_2 - \rho_3)^2 = \left(\frac{b_2}{v_2} - \frac{b_3}{v_3} \right)^2.$$

Note that the scattering cross section for **incompressible blends** is independent of the $(\rho_1 - \rho_2)^2$ contrast factor.

3. FITTING OF THE SANS DATA

The SANS data were fitted to the **RPA model for ternary blends** with the various known parameters (n_i , ϕ_i , v_i , $\Delta\rho_i^2$) with index i representing either dPS, hPS or PVME. The radii of gyration R_{gdPS} , R_{ghPS} and R_{gPVME} and the Flory-Huggins interaction parameters $\chi_{dPS/PVME}/v_0$, $\chi_{hPS/PVME}/v_0$ and $\chi_{dPS/hPS}/v_0$ were allowed to vary during the nonlinear least-squares fits.

The various **contrast factors** are:

$$\left(\frac{b_{hPS}}{v_{hPS}} - \frac{b_{PVME}}{v_{PVME}} \right)^2 N_{av} = 1.79 * 10^{-4} \text{ mol/cm}^4 \quad (7)$$

$$\left(\frac{b_{dPS}}{v_{dPS}} - \frac{b_{PVME}}{v_{PVME}} \right)^2 N_{av} = 6.07 * 10^{-3} \text{ mol/cm}^4$$

$$\left(\frac{b_{dPS}}{v_{dPS}} - \frac{b_{hPS}}{v_{hPS}} \right)^2 N_{av} = 4.16 * 10^{-3} \text{ mol/cm}^4.$$

Only two of these contrast factors are needed. Note that deuteration enhances the contrast factor and that Avogadro's number N_{av} has been introduced to keep from handling very small numbers.

Results of the fits are included here. The binary dPS/PVME blend (sample 1) gave a reliable estimate of the Flory-Huggins interaction parameter:

$$\left(\frac{\chi}{v_0} \right)_{dPS/PVME} = 9.73 * 10^{-4} - \frac{0.416}{T}. \quad (8)$$

This interaction parameter decreases with inverse temperature ($1/T$) which is a signature of the LCST behavior.

Previous measurements from a dPS/hPS binary blend and these measurements from ternary blends yielded:

$$\left(\frac{\chi}{v_0}\right)_{\text{dPS/hPS}} = -2.9 * 10^{-6} + \frac{0.0020}{T}. \quad (9)$$

This interaction parameter for an isotopic blend is orders of magnitude smaller than typical ones for other blends. It increases with $(1/T)$ which means that the dPS/hPS is characterized by a UCST behavior.

The third interaction parameter obtained from fits of the data taken from samples 2 and 3 are:

$$\left(\frac{\chi}{v_0}\right)_{\text{hPS/PVME}} = 10.3 * 10^{-4} - \frac{0.422}{T} \quad \text{from sample 2} \quad (10)$$

$$\left(\frac{\chi}{v_0}\right)_{\text{hPS/PVME}} = 10.6 * 10^{-4} - \frac{0.436}{T} \quad \text{from sample 3.}$$

These values agree fairly well. The units of (χ/v_0) are in cm^3/mol .

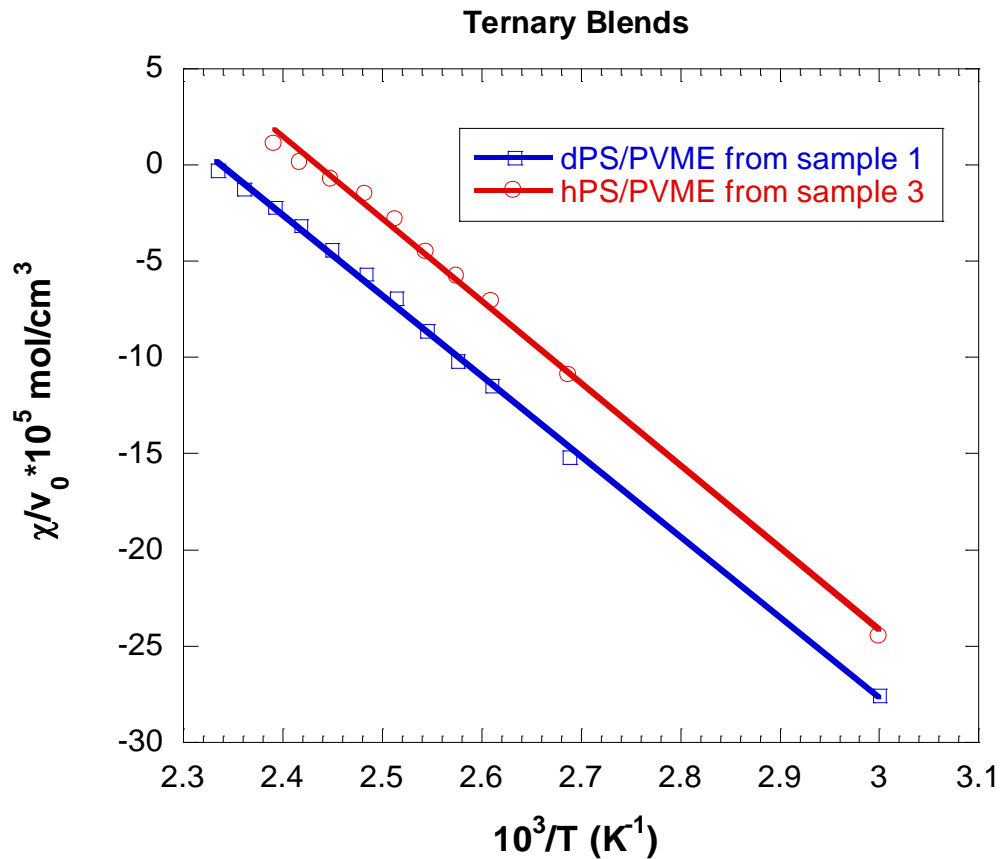


Figure 3: Variation of the Flory-Huggins interaction parameters for dPS/PVME obtained from sample 1 and for hPS/PVME obtained from sample 3.

The interaction parameters for the dPS/PVME and the hPS/PVME are close but not identical. The difference is due to the isotopic effect.

4. SPINODAL TEMPERATURE

The spinodal temperature is reached when the denominator of the structure factors in the thermodynamics limit (i.e., for $Q = 0$) goes to zero.

$$(1 + v_{11}S_{11}^0(0))(1 + v_{22}S_{22}^0(0)) - v_{12}^2 S_{11}^0(0)S_{22}^0(0) = 0. \quad (11)$$

This gives the following estimates for the spinodal temperatures:

$$T_s = 433 \text{ K} = 160 \text{ }^\circ\text{C} \text{ for Sample 1}$$

$$T_s = 421 \text{ K} = 148 \text{ }^\circ\text{C} \text{ for Sample 2}$$

$$T_s = 416 \text{ K} = 143 \text{ }^\circ\text{C} \text{ for Sample 3.}$$

Note that this method is based on estimating the spinodal temperature from the one-phase (i.e., mixed phase) region.

5. DISCUSSION

Using ternary blend mixtures allowed measurement of the Flory-Huggins interaction parameter for a pair of non-deuterated polymers (hPS/PVME). This binary blend mixture could not have been measured directly by SANS due to the very small contrast factor and to the overwhelming incoherent scattering background. The method presented here is a reliable method to measure the small isotopic effect on the polymer-polymer interaction parameter.

The phase diagram for a ternary blend mixture can be represented by a triangle with the three components at the corners and temperature as the vertical axis (out of the page where the triangle is drawn).

When supplemented with the RPA model, the SANS technique is useful for the investigation of the demixing (i.e., spinodal) phase transition. This method has been used to investigate many homogeneous polymer mixtures.

REFERENCES

B. Hammouda, R. Briber and B. Bauer, "SANS from dPS/PVME/hPS Ternary Polymer Blends", *Polymer* 33, 1785-1787 (1992).

QUESTIONS

1. How does the scattering intensity vary for increasing temperature for a Lower Critical Spinodal Temperature (LCST) polymer blend mixture? How about for an Upper CST?
2. In the Random Phase Approximation (RPA) model, what is the size of the matrices for an incompressible ternary polymer blend?
3. Does the RPA model apply in the two-phase (i.e., phase separated) region?
4. Using the RPA model, could one work out the phase diagram for a ternary blend mixture?

ANSWERS

1. The scattering intensity increases for increasing temperature for an LCST polymer blend. The scattering intensity decreases for increasing temperature for a UCST blend. The scattering intensity always increases when approaching the spinodal temperature due to the buildup of composition fluctuations.
2. A ternary polymer blend contains three components. The incompressibility assumption allows the elimination of one component (referred to as the “background” component). Therefore, the size of the RPA matrices is two.
3. The RPA model does not apply in the two-phase region. It applies only in the homogeneous (i.e., mixed phase) region and breaks down at the spinodal line.
4. The RPA model could be used to map out the phase separation lines (spinodal temperatures) for a ternary blend mixture. The phase diagram is triangular with one component at each corner and temperature as the third dimension.